RESIN COMPOSITION SUITABLE FOR PRINTING AND PRINTING METHODS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is the U.S. national phase of International Application No. PCT/EP2019/069338 filed 18 Jul. 2019 which designated the U.S. and claims priority to British Patent Application No. 1811896.8 filed 20 Jul. 2018, the entire contents of each of which are hereby incorporated herein by reference.

FIELD OF THE INVENTION

[0002] Embodiments of the invention relate to a resin composition, in particular suitable for printing, a kit comprising components of the resin composition, printing methods, a polymer obtained by the printing methods, an article comprising or formed from the polymer, uses thereof, and a composition.

BACKGROUND

[0003] Printing methods may serve for a large variety of purposes. In addition to traditional two-dimensional printing methods that are still widely used, three-dimensional printing methods have gained increasing interest over the past years. Initially developed for preparing prototypes, for instance for design purposes, three-dimensional (3D) printing methods are now more and more utilized for producing highly sophisticated and complex geometric structures that are brought to market as such, for instance in the automobile industry, for producing ornaments and in end-user appliances (Wendel et al., Macromol. Mater. Eng. 293 (2008) 799-809).

[0004] Among the known 3D printing methods, stereolithography (SLA) represents a very promising approach, since it attains a very high resolution that can hardly be attained with other techniques. This technique based on photopolymerization of liquid resins has a great potential for the manufacture of tailored shaped articles for the producing industry (among others, automotive, aviation, medical field) requiring a high fitting accuracy as well as high surface quality. However, the hitherto used materials in stereolithography do often not fulfill the required thermo-mechanical properties and are often brittle compared with technically relevant plastic materials (Ligon-Auer et al., Polym. Chem. 7 (2016) 257). Thus, they may be applied in prototyping, but the application of the produced shaped articles as fully operable parts is limited. In addition, commercially available resin compositions are mainly based on (meth)acrylate monomers, which are not suitable for the production of medical devices to be contacted with tissue due to their cytotoxicity (HusAr et. al, J. Polym. Sci. A Polym. Chem. 49 (2011) 4927).

[0005] Thus, the choice of commercially available printing resins suitable for stereolithography is still limited so that there is a need for the development of new materials and compositions.

OBJECTS OF THE INVENTION

[0006] In light of the foregoing, embodiments of the invention invention aims at overcoming the above described problems and drawbacks of hitherto available printing resins, in particular the restrictions thereof in terms of thermo-mechanical properties and suitability for use in medical or biomedical appliances. Thus, there may be a need to provide a novel resin composition which may be suitable for printing, in particular by means of stereolithography, and which may provide tailored shaped articles meeting the requirements of the producing industry in terms of thermo-mechanical properties, such as ductility, low shrinkage, dimensional stability under heat, and/or biocompatibility for medical or biomedical applications. Moreover, there may be a need to provide a procedure for cleaning 3D printed structures by means of completely removing residuals of non-cured UV resin without risk of deterioration of the printed structures.

SUMMARY OF THE INVENTION

[0007] The inventors have made diligent studies for solving these objects and have found that a resin composition comprising three types of monomers, namely a compound having a terminal alkyne functional group, a compound having at least two thiol functional groups and a compound having a carbon-carbon double bond, i.e. a thiol-yne-alkene system, may be polymerized in a thiol-yne-alkene reaction during a printing process upon irradiation in the presence of a photoinitiator and under high monomeric conversion (>90%) such that the resulting polymer may form a three-dimensional network having high homogeneity which may exhibit unique thermo-mechanical characteristics, such as a high ductility, a very good dimensional stability under heat and even a shape memory behaviour, as well as excellent biocompatibility and biodegradability (as appropriate), further offering the possibility of applying antimicrobial (nano) coatings. In particular, the inventors have found that the advantageous characteristics resulting from a step-growth polymerization, as it is the case in a thiol-yne reaction, such as a low shrinkage stress (resulting in a less brittle polymer article), and the advantageous characteristics resulting from a chain-growth polymerization, as it is the case in a radical alkene polymerization, such as an adjustable time of gelation, in particular a sufficiently short time of gelation appropriate for 3D printing, may be achieved in combination in a thiol-yne-alkene system, as described herein. Noteworthy in this regard, a low shrinkage stress and a short time of gelation are typically conflicting properties. In a mere thiol-yne system, the gel point is achieved at a relatively late stage of the polymerization reaction due to the step-growth mechanism, which enables that the shrinkage stress may be substantially relieved (thus, the resulting polymer may exhibit a low shrinkage stress), but which also leads to very long printing times. On the other hand, in a mere radical alkene polymerization, for instance when polymerizing pure (meth)acrylates, the gel point is achieved very quickly due to the chain-growth polymerization mechanism, so that very fast printing times may be realized, but very high shrinkage stress is generated in the network thus formed, so that the polymers tend to become brittle. The inventors have found that in a thiol-yne-alkene system, as described herein, both mechanisms may be combined enabling an adjustable time of gelation as well as superior (compared with a thiol-ene reaction) and also adjustable mechanical properties (such as heat deflection temperature (HDT) and modulus, see Examples 2 and 9). In addition, to maintain an appropriate viscosity so as to increase the storage stability, a stabilizer (in particular a combination of specific stabilizers) may be added to the resin composition. The inventors have further